V.2 High Temperature Electrochemistry Center

LR Pederson (Primary Contact), GW Coffey, OA Marina, GL McVay, CD Nguyen, PC Rieke, SC Singhal, and EC Thomsen
Pacific Northwest National Laboratory
Richland, Washington 99352
Phone: (509) 375-2731; Fax: (509) 375-2167; E-mail: larry.pederson@pnl.gov

LH Spangler, M Deibert, H Gao, VI Gorokhovsky, YU Idzerda, MH Nehrir, VH Schmidt, SR Shaw, and RJ Smith
Montana State University
Bozeman, Montana 59717

ED Wachsman, KL Duncan, F Ebrahimi, X Guo, KS Jones, JC Nino, SR Phillpot, H-J Seifert, WM Sigmund, and SB Sinnott
University of Florida
Gainesville, Florida 32611

AV Virkar
University of Utah
Salt Lake City, Utah 84112

DOE Program Manager: Lane Wilson
Phone: (304) 285-1336; E-mail: Lane.Wilson@netl.doe.gov

Objectives

- Objectives of the High Temperature Electrochemistry Center are to advance solid oxide technology, such as solid oxide fuel cells (SOFCs), high temperature electrolyzers, reversible fuel cells, energy storage devices, gas separation membranes, and electrochemical sensors, for use in distributed generation and FutureGen applications, as well as to conduct fundamental research that aids the general development of all solid oxide technology.

Approach

- Develop reversible solid oxide fuel cell technology capable of efficiently producing hydrogen in an electrolyzer mode as well as producing electrical power from stored hydrogen in the fuel cell mode.
- Develop high temperature ceramic membranes for separating hydrogen from gasified coal and other complex mixtures.
- Advance the fundamental understanding of reactions and processes that occur at the electrode-electrolyte-gas interface, critical to the operation of a wide range of electrochemical technologies including fuel cells, electrolyzers, sensors, and gas separation membranes.
- Develop model corrosion-resistant, multilayer thin films aimed at extending the lifetime of metallic fuel cell interconnects.
- Develop tools necessary to monitor and model the response of fuel cells to transient electrical loads, and design power electronics modules to improve the performance and efficiency of fuel cells integrated with multiple power sources.
- Develop simulation methods to provide insight on ion and electron transport mechanisms, the structure and thermodynamic properties of vacancy clusters, and oxygen reactions at surfaces and interfaces.

Accomplishments

- A ceramic fuel electrode consisting of doped strontium titanate and doped ceria shows high activity for steam electrolysis and is electrically conductive. Doping of cerate phase with Group Va metals significantly enhances the catalytic activity for both steam electrolysis and hydrogen oxidation. Lower polarization losses associated with the ceramic composite electrode can lead to more efficient hydrogen production by steam electrolysis.
- Thin composite barium zirconium cerate/nickel membranes with submicron grain structures have been prepared on a porous support, intended to passively separate hydrogen from an impure mixture such as coal gas. The thin, supported structure provides enhanced transport while maintaining good mechanical properties.
- Copper-substituted lanthanum ferrite air electrodes have been developed that are exceptionally active at low temperature, but approximately equal to lanthanum ferrites at higher temperatures. Investigations of electronic and ionic conductivity, carrier density, oxygen content, electrode polarization and other properties have shown that copper is susceptible to reduction, leading to diminished activity.
- University of Utah and Pacific Northwest National Laboratory (PNNL) researchers have used cells with patterned electrodes to develop insights into the mechanism of the air electrode reaction. For platinum and lanthanum manganite electrodes, the charge transfer resistance was found to vary inversely with the length of the triple phase boundary for purely electron-conducting electrodes, thus confirming the validity of this novel experimental approach. Such information is critical in enabling cathode compositions to be optimized.
- Synchrotron radiation has been used by researchers at Montana State University (MSU) to examine reactions occurring at a buried electrode-electrolyte interface. By using polarization-dependent X-ray absorption spectroscopy (XAS), the chemical state of different elements of $La_XCa_{1-x}MnO_3$ (LCM) was shown to change as a function of the stress within the LCM film. These studies are expected to provide unique insight into reactions and processes that control the activity of fuel cell electrodes.
- In collaboration with the University of Missouri-Rolla, anomalous shrinkage behavior of porous Sr-doped lanthanum manganite has been found, occurring at temperatures hundreds of degrees lower than the sintering temperature. The mechanism for shrinkage is attributed to be enhanced metal ion diffusion in a vacancy gradient imposed by thermal and oxygen partial pressure cycles.
- Large area filtered arc deposition (LAFAD) has been utilized at MSU to fabricate multilayer coatings on steel coupons as a means of improving high temperature corrosion resistance through surface engineering. An order of magnitude improvement in oxidation resistance of 440 stainless steel was achieved by applying nanolayered coatings of CrAlON. The coating technology offers promise for extending the life of steel SOFC interconnects.
- Scale-up of the LAFAD process to apply corrosion-resistant coatings to interconnect plates of a size compatible with Solid State Energy Conversion Alliance (SECA) stack designs has been demonstrated at MSU. Uniform, nearly defect-free multilayer coatings were prepared on steel plates that were 10 cm by 10 cm in size.
- An electrical circuit based model for a fuel cell system has been developed and used in modeling and control of stand-alone and grid-connected distributed power generation systems. The control strategies developed could result in improved performance of grid-connected and stand-alone hybrid fuel cell power plants.
- A low-cost, high-efficiency DC-DC converter for residential fuel cell power generation systems has been designed and simulated. A scale-down prototype has been built. Preliminary experimental results show the validity of this unique approach to the current DC-DC converter design.
- A non-intrusive load monitor has been developed at MSU that can disaggregate currents measured at a central location and is capable of associating disaggregated current transients with individual loads. This

technology provides a useful tool for studying fuel cell models under real-world use conditions, for surveying the load served by the fuel cell, and for characterizing fuel-cell load interactions.

- A transient recognition control (TRC) predictive model that can recognize and respond to electrical load transients has been developed at MSU. The predictive modeling approach has been validated and appears to be useful for hybrid fuel cell systems.

Future Directions

- Develop an efficient reversible fuel cell with air and fuel electrode compositions and forms to minimize overpotential losses. Establish operating conditions leading to most efficient operation.
- Develop composite hydrogen separation membranes aimed at meeting the DOE Office of Fossil Energy's (FE's) targets for permeation and strength.
- Employ filtered arc plasma methods to deposit high-quality Mn-Co-O spinel films intended to enhance the corrosion resistance of metallic interconnects. Establish oxygen and chromium migration rates through these dense coatings. Investigate the applicability of filtered arc methods to prepare thin film fuel cell structures for intermediate temperature operation.
- Apply advanced X-ray techniques to study the oxygen reduction and oxygen ion oxidation mechanisms at the electrode/electrolyte interface at high temperature.
- Demonstrate the efficacy of cluster training methods in enhancing the transient load following of a solid oxide fuel cell system.
- Conduct fundamental research on the mechanisms of ionic transport in solids, combining experimental measurements with molecular dynamics and electronic structure simulation. Investigate the relation between external environment and mechanical properties through defect equilibria modeling.
- Use controlled microstructure processing methods to tailor the microstructure and composition of the solid electrolyte/electrode interface.

Introduction

The High Temperature Electrochemistry Center (HiTEC) was created in 2002 to provide crosscutting, multidisciplinary research that supports the Office of Fossil Energy's FutureGen Initiative. The National Energy Technology Laboratory (NETL), Montana State University (MSU), the University of Florida, the University of Utah and the Pacific Northwest National Laboratory (PNNL) currently are contributors to HiTEC. Objectives of the High Temperature Electrochemistry Center are to advance solid oxide technology, such as solid oxide fuel cells, high temperature electrolyzers, reversible fuel cells, energy storage devices, gas separation membranes, and electrochemical sensors, for use in distributed generation and FutureGen applications, as well as to conduct fundamental research that aids the general development of all solid oxide technology.

A broad range of research topics are currently being addressed. Current research activities being conducted at PNNL include the development of low-loss electrodes for reversible solid oxide fuel cells, the development of high temperature membranes for hydrogen separation, fundamental electrode reaction mechanism studies, and development of computational tools relevant to high temperature electrochemical systems. Research activities at MSU include the development of dynamic models of fuel cell systems for distributed generation applications, development of adaptive power controllers for fuel cells, development of multilayer thin film coatings to improve the corrosion resistance of interconnect materials, research on transport in hydrogen separation membranes, and advanced x-ray studies of buried interfaces. Research activities at the University of Florida include fundamental ion transport mechanisms investigation, development of electronic structure and molecular dynamics tools to study ion transport, microstructural characterization of model interfaces, studies of the relation of environment to thermo-mechanical properties, advanced synthetic research to provide tailored microstructures, and computational and experimental investigations of the thermodynamic properties of high temperature fuel cell materials.

Results

Improved efficiency through lowered electrode polarization losses of a reversible solid oxide fuel cell is among the goals of this project. A composite consisting of doped strontium titanate and doped ceria is being developed for use as the fuel electrode. Good electronic conductivity is provided by lanthanum-doped $SrTiO_3$, an *n*-type semiconductor under reducing conditions, while the cerate phase doped with Group Va metals significantly enhances the catalytic activity for both steam electrolysis and hydrogen oxidation. Because this electrode is composed of metal oxides, it is less susceptible than nickel/zirconia to degradation by intermittent exposure to air. Lower polarization losses associated with the ceramic composite electrode can lead to more efficient hydrogen production by steam electrolysis.

Titanate/ceria composite electrodes exhibited promising polarization losses under both cathodic and anodic conditions, but operated most efficiently in the electrolysis mode. Polarization curves for a $La_{0.35}Sr_{0.65}TiO_{3-}$ -$Ce_{0.99}Nb_{0.01}O_{2-}$ in a 1:1 mole ratio electrode at different partial pressures of steam at 850°C are shown in Figure 1. Cell current densities increased with increased steam partial pressures at a constant initial hydrogen partial pressure in the electrolysis mode. In the fuel cell mode, cell current densities were insensitive to the steam partial pressure. The ceramic composite anode requires a minimum hydrogen partial pressure to operate efficiently, as shown in Figure 2. With insufficient hydrogen present, slow oxidation of the ceria led to higher polarization losses. Current densities were stable when sufficiently reducing conditions were maintained.

Copper-substituted lanthanum strontium ferrites have been shown to be exceptionally active as the air electrode in a reversible solid oxide fuel cell, though they perform similarly to lanthanum strontium ferrite at temperatures greater than ~800°C. The tendency for copper to be reduced in the perovskite at high temperatures and in low oxygen concentrations is at least partially responsible for such behavior. In Figure 3, the four-point electrical conductivity of LSCF-7337 versus temperature in varied oxygen concentrations shows a maximum at ~550°C and diminishes considerably as the oxygen concentrations are lowered. In contrast, LSF-30 shows only a small dependence on the oxygen concentration from 1 to 100% oxygen. Copper-substituted lanthanum strontium ferrites show high mixed electronic and ionic conductivity, which enhances electrocatalytic activity through extension of the dimensions of the triple phase boundary. Transference numbers for oxygen ions for a series of copper-substituted lanthanum strontium ferrites are given in Figure 4 versus temperature, where oxygen ion conductivities were determined by permeation.

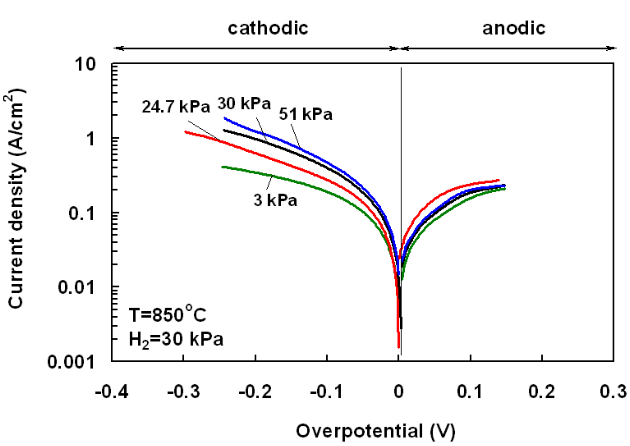

Figure 1. Polarization curves for a $La_{0.35}Sr_{0.65}TiO_{3-}$ - $Ce_{0.99}Nb_{0.01}O_{2-}$ in a 1:1 mole ratio electrode at different partial pressures of steam at 850°C. Polarization losses decreased with increased steam concentration in the electrolysis mode.

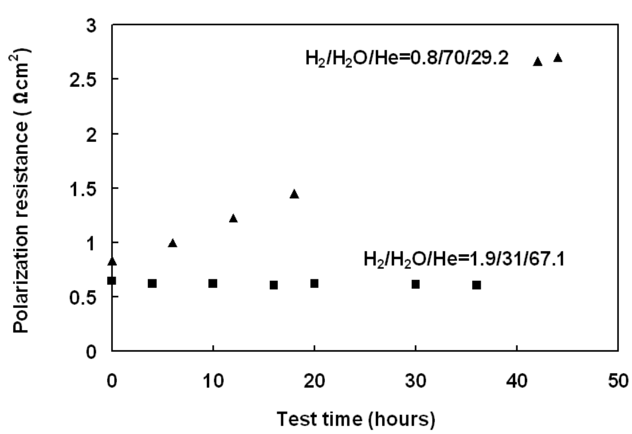

Figure 2. Durability test on $La_{0.35}Sr_{0.65}TiO_{3-}$ - $Ce_{0.99}Nb_{0.01}O_{2-}$ anode, 1:1 mole ratio, at different partial pressures of hydrogen at 900°C. The more oxidizing conditions led to a loss of electrical conductivity and electrode activity with time.

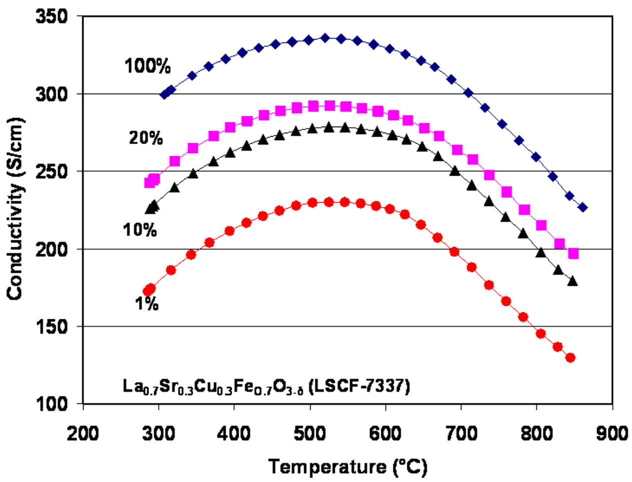

Figure 3. Electrical conductivity of LSCF-7337 versus temperature in varied oxygen concentrations. Copper reduction at high temperatures and low oxygen concentrations leads to a loss of electrical conductivity.

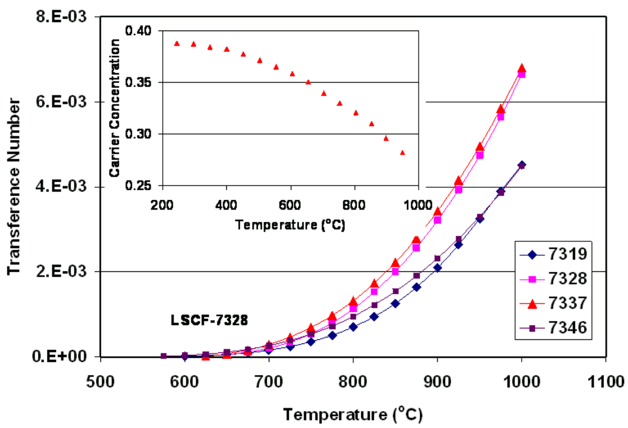

Figure 4. Transference numbers for oxygen ion conductivity for a series of copper-substituted lanthanum strontium ferrites. Oxygen ion conductivities were determined by permeation. The inset shows electronic carrier concentration as a function of temperature in air calculated from the Seebeck coefficient.

Oxygen ion conductivity contributes approximately 0.1% to the overall conductivity at 800°C, with the fraction rising with increased temperature. The inset in Figure 4 shows that the electronic carrier concentration, determined from the Seebeck coefficient, decreases significantly with increased temperature. Thus, while the copper-substituted ferrites are found to be very active electrocatalysts, they are most suited for intermediate or low temperature operation.

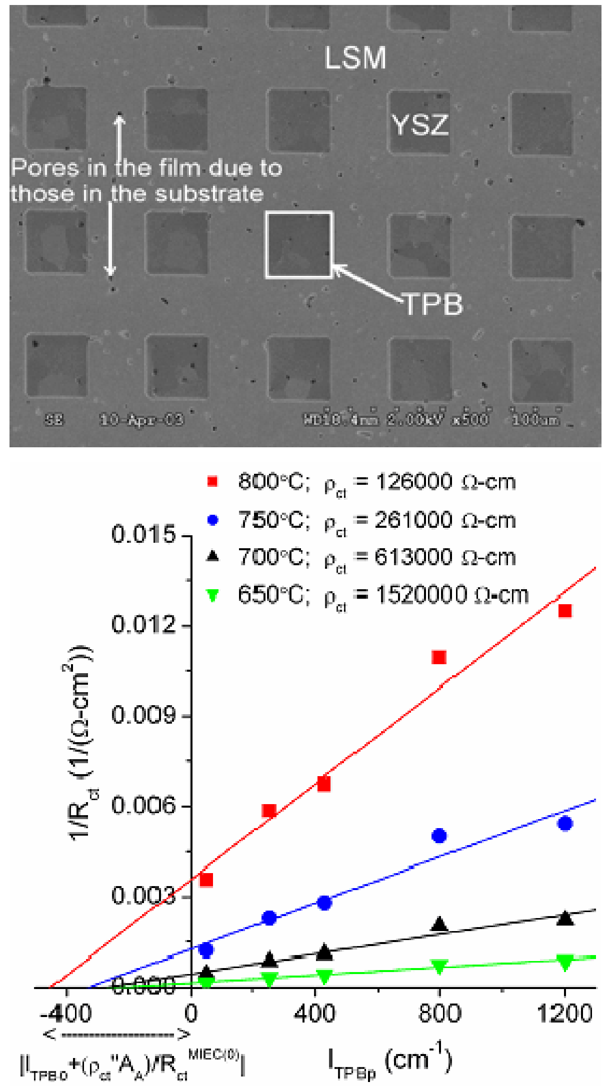

Figure 5. Estimation of the charge transfer resistivity of $La_{0.8}Sr_{0.2}MnO_3$ cathodes on 8YSZ electrolyte using patterned electrodes. By varying the geometric length of the triple phase boundary while maintaining the electrode area constant, University of Utah and PNNL researchers showed a linear dependence of 1/charge transfer resistivity on triple phase boundary length. Similar results were found for platinum.

To better understand the mechanisms of cathodic reactions, University of Utah and PNNL researchers have prepared novel, patterned electrode-electrolyte structures using lithographic techniques. These structures provide a well-defined triple phase boundary length, thus allowing intrinsic electrocatalytic activity to be determined without ambiguity. Figure 5 shows typical electrode design and includes charge transfer resistivity results as a

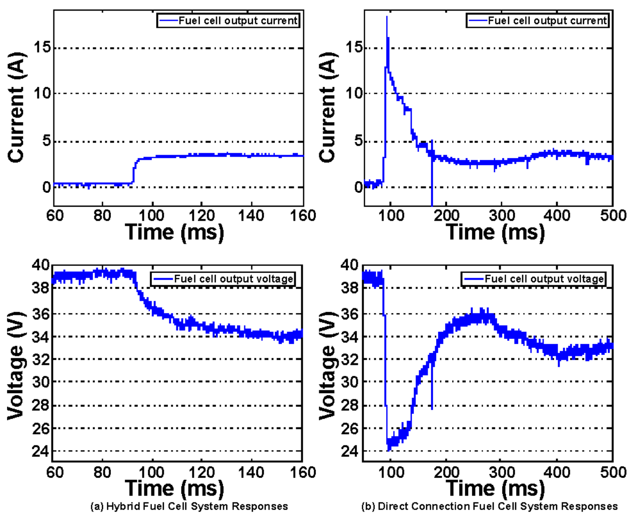

Figure 6. TRC technology has been developed at MSU, aimed at enabling a fuel cell system to recognize and respond to characteristic transients introduced by various appliances. Concepts were demonstrated using off-the-shelf electronics and a 500 We fuel cell. Figure 6a shows current and voltage response of the fuel cell to an incandescent light bulb being switched on. Figure 6b shows the instability of that same system to the same transient load without TRC.

function of geometric triple phase boundary length. Yttria-zirconia discs with patterned platinum, lanthanum strontium manganite, and lanthanum strontium cobaltite electrodes having three different triple phase boundary lengths but having the same macroscopic electrode-electrolyte interface areas were prepared and studied by electrochemical impedance spectroscopy. The charge transfer resistance was found to vary inversely with the length of the triple phase boundary for purely electron-conducting electrodes such as platinum and lanthanum strontium manganite, thus confirming the validity of this novel experimental approach. This relation did not hold for mixed conductors such as lanthanum strontium cobaltite. Such information is critical in enabling cathode compositions to be optimized.

A transient recognition control (TRC) predictive model has been developed at MSU that can recognize and respond to electrical load transients. A cluster-weighted modeling algorithm was utilized to build the electrical load transient recognition model.

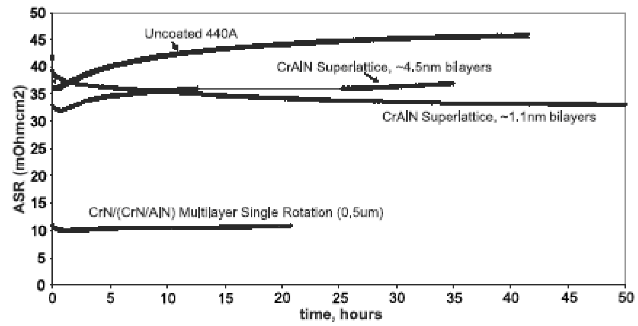

Figure 7. Area-specific resistances of coated and uncoated 440A stainless steel exposed to air at 800°C. Multilayer coatings consisting of alternating layers of chromium nitride and aluminum nitride deposited by filtered arc plasma methods resulted in improved ASR values for various steels. The technology may lead to improved performance of metal interconnects in solid oxide fuel cells.

Transient recognition control concepts have been simulated using MATLAB and demonstrated using off-the shelf power electronics and a 500 We fuel cell, as shown in Figure 6 for a transient electrode presented by turning on an incandescent light bulb. Figure 6a shows current and voltage response of the fuel cell to an incandescent light bulb being switched on. In this case, stack output currents and potentials became stable typically in less than 10 milliseconds. Figure 6b shows the instability of that same system to the same transient load without TRC control, where oscillations persisted for hundreds of milliseconds. The predictive modeling approach has been validated and appears to be useful for hybrid fuel cell systems.

Multilayer coatings consisting of alternating layers of chromium nitride and aluminum nitride were deposited onto 304 and 440 stainless steels and onto Crofer grade APU 22. After exposure to air at 800°C for varying periods, the corrosion layer was analyzed by Rutherford backscatter, nuclear reaction analysis, x-ray photoelectron spectroscopy, analytical electron microscopy, and atomic force microscopy. Changes in area specific resistance (ASR) due to exposure to air at high temperatures were also assessed. Both the short-term oxidation resistance and the ASR growth rate were improved significantly for some of the coated coupons. Results for a 440A martensitic stainless steel are given in Figure 7 for exposure of coated and uncoated coupons to air at

800°C. Best ASR values obtained for these coatings were approximately 10 m-ohm cm^2, which is significantly lower than that of the uncoated specimen. This technology holds significant promise for enabling the use of metallic interconnects in solid oxide fuel cells.

Conclusions

- Composite ceramic electrode compositions have been developed that show high activity for steam electrolysis.
- Copper-substituted lanthanum strontium ferrites were shown to be highly active fuel cell cathodes. The tendency for copper reduction limits application to intermediate temperature fuel cells.
- Charge transfer resistance for purely or nearly purely electronic conductors has been shown to be related to the geometric triple phase boundary length in studies utilizing patterned electrodes. The studies provide insight into the mechanism of oxygen reduction in fuel cells.
- Transient recognition control methodology has been developed that allows fuel cell systems to respond to transient electrical loads. The validity of the approach was demonstrated with a 500-watt fuel cell and off-the-shelf electronics.
- Filtered arc plasma has been applied to deposit multilayer metal nitride coatings. The coatings have resulted in substantial improvements in both the initial ASR as well as the growth in that value with long-term exposure to air at high temperatures.

FY 2005 Publications

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